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PROCESS FOR THE PREPARATION OF METAL OXIDES THAT ARE
DISPERSIBLE IN ORGANIC SOLVENTS

- 5 This invention relates to a process for preparing metal
oxides or metal aquoxides that are dispersible in organic
solvents. The invention further relates to metal oxides
or metal aquoxides that are modified with organic sul-
fonic acids and can be prepared by this process.
- 10 From WO 95/12547 or German patent DE 43 37 643-C1, a pro-
cess is known for the preparation of nanocrystalline alu-
mina hydrates in boehmitic or pseudoboehmitic form that
are dispersible in water. Water-dispersible alumina hy-
15 drates can be obtained in this process by hydrolysis of
aluminum alkoxides at temperatures from 30°C to 110°C,
addition of an acid (monovalent inorganic or organic
acids as well as their anhydrides), and subsequent hydro-
thermal aging. The resultant suspensions are suitable for
20 example for coating materials, such as glass, metal, or
plastics, as well as for producing high-strength catalyst
supports, pure-phase mixed oxides, or after conversion to
the α -form, for producing high-performance abrasives. The
water-dispersibility of those alumina hydrates, which are
25 not dispersible in organic solvents, is a disadvantage
for certain applications, such as weather-resistant ex-
terior coatings. For certain applications, aluminas that
are dispersible in organic solvents but not in water are
of interest.
- 30 The aluminas prepared by some of the processes known in
the art are dispersible in dilute acids and water, and
some of these aluminas are dispersible in short-chain
alcohols, such as methanol and ethanol. They are not
35 dispersible in organic aprotic solvents.

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- Colloidal alumina solutions in organic solvents are described for example in DE 41 16 522-C2 as well as by R. Naß and H. Schmidt ("Formation and Properties of Chelated Aluminum Alkoxides" in H. Hauener, G. Messing, S. Hirano (Eds.) "Ceramic Powder Processing", Deutsche Keramische Gesellschaft, Cologne, 1969). According to said publication, the alumina hydrates obtained by hydrolysis of aluminum alkoxides in an organic solvent and in the presence of a β -diketone compound can occur as colloids in the solvent. However, the colloidal solutions described there are only (meta)stable in the organic solvent at high dilutions. Only for isopropanol as a solvent has it been experimentally proven that the solutions are in fact colloidal ones. Experiments have shown that after removal of the solvent, the colloidal particles prepared by said process cannot be redispersed.
- From AU 200149 a process is known for the preparation of various inorganic oxides and hydroxides that can be dispersed in mineral oils. For this purpose, inorganic oxides or hydroxides are subjected to grinding in a ball mill in the presence of a surfactant and a mineral oil as the carrier fluid. As surfactants, organic sulfonic acids are cited among others. The surfactants are added to the composition in quantities of 0.5 to 3 wt%.

- In US 3,018,172, a process is described for the preparation of aluminum hydroxides that are dispersible in non-polar, high-molecular organic solvents, such as mineral oils. In said process, aluminum alkoxides in a volatile organic solvent are hydrolyzed by contact with an organic sulfonic acid, such as postdodecylbenzenesulfonic acid in

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a viscous organic carrier fluid. After hydrolysis, the volatile organic solvent is removed and an aluminum hydroxide dispersed in a viscous organic carrier fluid, such as xylene, remains.

A similar process is described in US 3,867,296, wherein a high-molecular organic sulfonic acid in a viscous organic carrier fluid is added to alumina hydrates in a volatile organic medium.

US 4,076,638 and US 4,123,231 describe variants of this process. According to US 4,076,638, a carboxylic acid is used in parallel, while the viscous organic carrier fluid is dispensed with. According to US 4,123,231, an aqueous mineral acid is used in addition to the organic sulfonic acid.

The processes described in the aforementioned U.S. patents have in common that substantial amounts of organic sulfonic acids must be used compared to the amount of alumina hydrate. In addition, organic solvents are required for the preparation of dispersible alumina.

According to AU 200149, mineral oxides are taken up in highly viscous mineral oils having a high solids content and then are dispersed in mineral spirits at high dilutions with a low solids content. However, these are no real colloidal solutions.

After drying, the products obtained by the aforesaid processes are no longer dispersible in organic solvents. It is the object of the present invention to provide dispersible metal oxides/metal aquoxides. It is a further

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object of this invention to provide a process for preparing such products, which does not have the disadvantages of the prior art and, for example, does not require organic solvents for their preparation. These problems are solved by the subject matter of the invention.

The subject matter of the present invention is a process for preparing metal oxides or metal aquoxides, especially alumina hydrates that can be dispersed in protic or aprotic organic solvents. Said products can be obtained by reaction of

- (A) one or a plurality of metal oxide(s)/metal aquoxide(s) having a crystallite size of 4 to 100 nm, preferably 6 to 20 nm (determined by x-ray diffraction on the 021 reflex) and a particle size of less than 1,000 nm, preferably 5 to 500 nm, most preferably 20 to 100 nm (determined by photon correlation spectroscopy (PCS) in the suspension prior to drying, for example during the production process)
- (B) one or a plurality of organic sulfonic acid(s), where
 - (i) in case the reaction takes place in a largely aqueous medium or in the absence of a diluent, the organic sulfonic acid is a mono-, di-, or trialkylbenzene sulfonic acid, wherein the alkyl residue(s) is (are) C₁ to C₆ alkyl residues, preferably C₁ to C₄ alkyl residues, and mono-C₁-alkylbenzene sulfonic acids or mono-C₃-alkylbenzene sulfonic acids are preferred, or
 - ii) in case the reaction takes place in the presence of an organic aprotic solvent or an organic protic solvent, the organic sulfonic

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acid has at least 14 carbon atoms, preferably at least 16, and at least one aromatic ring,

5 wherein the components (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, preferably from 95:5 to 80:20. Suitable organic protic solvents according to (ii) are for example alcohols, pre-
10 ferably C₂ to C₄ alcohols. Suitable aprotic solvents according to (ii) are for example aromatic hydrocarbons, such as toluene. In case the reaction is carried out in the presence of a largely aqueous medium, it is preferred that the organic sulfonic acid be soluble in the largely
15 aqueous medium.

Preferred embodiments are the subject matter of the sub-claims.

- 20 The solvents used as dispersants according to the invention are:
- (I) aprotic polar organic solvents
 - (II) protic polar organic solvents having at least two carbon atoms, or
 - 25 (III) nonpolar organic solvents.

Suitable aprotic polar organic solvents (I) include ketones, ethers, and esters, such as acetone, tetrahydrofuran (THF), methyl ethyl ketone, polyol ester, 1,6-
30 hexanedioldiacrylate, and dimethylsulfoxide (DMSO).

Suitable protic polar organic, optionally high-molecular, solvents (II) having at least two carbon atoms include alcohols, polyethers (with at least one free hydroxy
35 group), hydroxyalkyl esters, and hydroxyalkyl ketones, or carboxylic acids. Suitable alcohols include for example

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ethyleneglycol, C₃ to C₈ mono- or dihydroxy alcohols, such as propanols, butanols, pentanols, and hexanols.

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Suitable nonpolar organic solvents (III) are for example toluene and chlorobenzene.

The dispersible metal oxides or metal aquoxides obtain-
10 able by the process of the invention are powders that can be dispersed in the aforementioned solvents up to a solids content of 35 wt%. The particle size of the dispersed alumina hydrates is preferably from 20 to 1,000 nm (determined by PCS).

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In a preferred embodiment of the present invention, the metal oxides or metal aquoxides, especially amorphous or nanocrystalline alumina hydrates (with crystallite sizes of up to 100 nm, measured on the 021 reflex, and grain
20 sizes between 0.2 µm and 90 µm with particle sizes of 20 to 1,000 nm in the suspension) are mixed and stirred with 0.2 to 2 grams of p-toluenesulfonic acid monohydrate per gram of alumina or metal oxide or metal aquoxide, in each case calculated as metal oxide, at temperatures between
25 0 and 140°C for a period from 30 to 180 minutes, and are dried by spray drying, freeze drying, drying in supercritical solvents, filtration, or rotary drum drying. The resultant powder retains little water dispersibility (< 30 wt%) and is characterized by a very narrow grain
30 size distribution. The powder can be easily dispersed in the aforementioned organic solvents with particle sizes from 10 to 1,000 nm, preferably from 10 to 500 nm (measured in the suspension).

35 Part of the suspensions obtained in this way are translucent. They produce transparent coatings, for example on

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films/foils, glass, or similar surfaces. As a result of their dispersibility in organic solvents, the aluminas
5 modified in this way are suitable for incorporation into various water-insoluble polymers or lacquers/paints.

Most of the suspensions prepared in this way are opaque. They are characterized by excellent sedimentation and
10 centrifugation stabilities. Hence, they are genuine colloidal solutions. Another peculiarity is their redispersibility, especially after drying, in organic solvents, and the possibility of making stable suspensions with a high solids content (> 20 wt%). Surprisingly, the
15 metal oxides/metal oxide hydrates obtained by the process of the present invention remain dispersible in the aforementioned dispersants (I) to (III), even after drying and, optionally, after finishing and/or storage.

20 In contrast to suspensions of alumina hydrates in aqueous systems, the viscosity increases only slightly at the beginning and then remains constant after one day (see Fig. 1/1). No sedimentation occurs, even not after several weeks. Owing to these properties, the p-toluenesulfonic
25 acid-modified alumina hydrate of the invention is particularly easy to process and is most appropriate for making transparent coatings. Furthermore, it is useful as a filler in hydrophobic materials, such as PVC or lacquers/paints based on organic solvents.

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Dispersing Procedure

Into a beaker, there were placed 18 grams of solvent and, while stirring vigorously, 2 grams of modified alumina
35 hydrate were added in portions into the vortex within 1 to 5 minutes. The mixture was stirred for additional 10

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minutes. The resultant suspension had a solids content of 10 wt%. No sedimentation will occur with readily dispersible products. Dispersibility was determined by centrifugation of the suspension at 2,000 rpm (10 min), drying (at 120 °C), and weighing of the precipitate.

By the term 'dispersible metal oxides/metal aquoxides' employed herein especially those products are characterized which, when following the procedure described hereinbefore, remain in a dispersed state at ≥ 95 wt% or ≥ 98 wt%.

15 Example 1

20 grams of water-dispersible nanocrystalline alumina hydrate (crystallite size measured on the 120 reflex: 8-12 nm) (CONDEA product Disperal™ S), corresponding to 14.4 grams of Al_2O_3 , were dispersed in a solution of 4 grams of p-toluenesulfonic acid in 180 grams of demineralized water and heated to 90°C for 30 minutes with stirring, thereby adjusting the pH-value to 1.5 and moderately thickening the suspension. After cooling, the suspension was spray dried (inlet temperature 240 to 270°C, outlet temperature < 110 °C). A white odorless powder was obtained the properties and dispersibility of which are shown in Table 2 and Tables 1 and 4, respectively.

30 Example 2 (PTSA-Modified Silica Alumina)

Batch: 180 grams of demineralized water
4 grams of p-toluenesulfonic acid (PTSA)
20 grams of Siral™ 30 D

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A suspension of 20 grams of Siral™ 30 D was prepared in a solution of 4 grams of p-toluenesulfonic acid in 180 grams of demineralized water. The resultant yellowish sol-like suspension was spray dried. The C-value after drying was 8.61%. The powder was redispersible at 99% in water and ethanol. After solvent exchange, it was redispersible in hexanol and ethylene glycol, too.

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Example 3

4 grams of postdodecylbenzenesulfonic acid (Marlon™ AS-3) were dissolved in 180 grams of toluene. 20 grams of Disperal™ S were added. The mixture was stirred at 80°C for 30 minutes. The resultant yellowish sol with a solids content of approx. 10% contained aluminum oxide particles having a size of about 195 nm (measured by PCS). The sol was at 97.3% stable to centrifugation (10 minutes at 2,000 rpm). After removal of the solvent at 40°C/77 mbar, a yellowish crystalline powder was obtained which was redispersible in toluene, tetrahydrofuran (THF), butanol, methyl-tert-butyl ether (MTBE), and trichloromethane. In chlorobenzene, a translucent suspension can be obtained, which is not stable to centrifugation, however. The powder is 100% hydrophobic, i.e., dispersibility in water was reduced to 0% by reaction with Marlon™ AS-3. The organosols are characterized by their long-term stability to agglomeration. No increase in viscosity was observed after several days. The dispersibility of the powder is shown in Table 3.

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Table 1 Dispersibility in Various Organic Solvents

Solvent	Dispersibility (up to 10 wt% solids)	Particle Size [nm]	Transmission (0.1% solids) [%]	Remarks	Centrifugation Stability (2,000 rpm/10 min) [%]
Acetone	Yes (opaque)	80	80.8%	With 20% solids: thixotropic	94.2%
Ethanol	Yes	100	84.5%	-	98.0%
i-Propanol	Yes (limited)	-			Not determined
n-Butanol	Yes (opaque)	97			99.5%
Hexanol	Yes	335	65.8%	Thixotropic	84.8%
Ethyleneglycol	Yes (opaque)				
THF	Yes (opaque)	121			96.5%
DMSO	Yes (opaque)	104			95.0%
Chlorobenzene	By solvent exchange * (20% solids)	400		Low viscosity	99.5%
Dichloromethane	No	-			-
Toluene	By solvent exchange *	PCS not possible		Gelatinized	Not determined
1,6-Hexanediol- diacrylate	By solvent exchange *	-		Polymerized in UV	Not determined

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* At first dispersion in acetone, then addition of equal amounts of solvent (here: chlorobenzene), followed by displacement of the acetone by stirring with heating to 40 °C.

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Table 2 Physical Characteristics of the Powder

		9.1 wt% PTSA	16.8 wt% PTSA
Specific surface area (BET) (activated for 3 h at 250 °C)	[m ² /g]	-	135
Pore volume (0 - 1,000 nm pore diameter)	[cm ³ /g]	-	0.23
Average pore radius	[nm]	-	3.2
Al ₂ O ₃ content	[%]	-	66
C content	[%]	3.8	6.5
Particle size (dynamic laser scattering)		d ₁₀ : 0.7 d ₅₀ : 2.2 d ₉₀ : 8.6	d ₁₀ : 0.3 d ₅₀ : 1.2 d ₉₀ : 8.5

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Table 3 Dispersibility of Disperal™ S / Marlon™ AS-3 in Various Solvents

Solvent	Dispersibility [%]	Particle Size (PCS) [nm]	Transmission [%]
Toluene	95.5	166	63.7
THF	99.0	113	32.3
Butanol	99.0	130	44.5
MTBE	85	-	6.8
Trichloromethane	98.5	64	42.3

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Table 4 Dispersibility of Disperal™ PTSA in Solvents Mixtures (10 wt% Solids)

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Solvent	Ratio	Particle Size (PCS) [nm]	Centrifugation Stability (2,000 rpm/10 min) [%]
CHCl ₃ : MeOH	90 : 10	90	98
CHCl ₃ : MeOH	70 : 30	70	97
CHCl ₃ : MeOH	50 : 50	80	97.5
CHCl ₃ : MeOH	30 : 70	107	97.5
CHCl ₃ : MeOH	10 : 90	70	98.5
CH ₂ Cl ₂ : MeOH	90 : 10	97	98
CH ₂ Cl ₂ : MeOH	70 : 30	109	96
CH ₂ Cl ₂ : MeOH	50 : 50	103	96.3
CH ₂ Cl ₂ : MeOH	30 : 70	97	98.5
CHCl ₃ : Acetone	70 : 30	148	84
CHCl ₃ : Acetone	50 : 50	52	97.5